

PATENT SPECIFICATION

(11)

1 453 645

1 453 645

- (21) Application No. 8672/74 (22) Filed 26 Feb. 1974
 (31) Convention Application No. 345 440 (32) Filed 27 March 1973 in
 (33) United States of America (US)
 (44) Complete Specification published 27 Oct. 1976
 (51) INT. CL.² C02B 1/12
 B01D 9/04
 (52) Index at acceptance
 C1C 300 302 404 424 425
 B1G 11A 12 14A 9B

(19)



(54) APPARATUS AND METHOD FOR PURIFYING
 CONTAMINATED LIQUIDS BY FREEZE CRYSTALLISATION

(71) We, AVCO CORPORATION, of 1275 King Street, Greenwich, Connecticut 06830, United States of America, a Corporation organized and existing under the laws of the State of Delaware, United States of America, do hereby declare the invention, for which we pray that a patent may be granted to us and the method by which it is to be performed to be particularly described in and by the following statement:—

This invention is directed to apparatus for and methods of purifying contaminated water or other liquid solvents and simultaneously obtaining dissolved and/or suspended solids in a dry form by means of a two-step freeze crystallization process.

In known processes of this kind, as in the present invention, each such stage comprises a freezing step carried out in a freezer-crystalliser and producing a slurry of crystals of the solid solvent suspended in a concentrate of the liquid fed into the freezer-crystalliser, followed by a washing step carried out in a wash column into the lower region of which said slurry is fed while wash liquid is fed into the upper region and part of said concentrate is removed through a screen in an intermediate region. In the wash column the crystals of liquid solvent in the slurry coalesce to form a porous plug having said concentrate within its pores and this plug travels up through the column and an upper part of it is continuously removed from the column.

The method and apparatus of the invention overcome or reduce the serious problem which has been caused by the freezing of water or other liquid being purified on the screen of the wash column used for purification. This is done by a method in which the plug of ice or other solvent crystals in the second stage separation column is compacted as it is moving upwards in the column.

In the description which follows and in the claims the following definitions will apply where the context permits:

Contaminated solvent includes sea water, brackish water, industrial waste water, chemical process streams and water or other solvent liquids which contain salts or other chemicals or impurities in suspension or solution. Whilst the description will deal with aqueous solutions, the process and apparatus of the invention can also be used where non-aqueous solvents are involved providing that such solvents can be freeze crystallized.

The "concentrate" from a stage in the process of the invention is a liquid obtained by concentrating the liquid fed to that stage by removing part of the solvent therefrom with the effect of increasing the concentration of contaminant in the liquid remaining. Thus, the "first concentrate" is the liquid remaining when, in the first stage of the process, part of the solvent in the contaminated liquid constituting the feed liquor for the first crystalliser is removed from the solid phase by freezing. This first concentrate is formed in the first freezer crystalliser and is fed in admixture with the crystals of solid solvent formed in the freezing, the mixture being in the form of a slurry, into the first wash column wherefrom the major proportion of the first concentrate is drawn off through the screen thereof and solid solvent is separately removed from the column. Similarly, the "second concentrate" is the liquid remaining when, in the second stage, first concentrate fed to that stage is further concentrated by removing part of its solvent. The second concentrate, formed together with crystals of solid solvent in the second freezer crystalliser, is fed in admixture with those crystals to the second wash column, in which a major part of the second concentrate is drawn off through the

screen of the column and solid solvent is separately removed.

A "dilute concentrate" is one in which the concentration (expressed, for instance as parts by weight) of contaminants in solution and/or suspension is relatively low; a "concentrated concentrate" is one on which that concentration is relatively high.

Desalination of sea water by freeze crystallization process is known. Generally, freeze desalination is accomplished in a single stage apparatus. Where the freezing point of the slurry supplied to a wash column is less than about 24°F, a single stage freeze desalination apparatus breaks down because water freezes on the screen of the wash column. A frozen screen generally upsets the delicate balance of operating parameters of the wash column bringing the purification process to a halt.

Known methods of keeping the screen from freezing, such as heating the screen, fall short of practicability because the power required to prevent the freezing is a serious burden on the overall efficiency of the apparatus. In an extreme case, it may not be possible to reliably prevent freeze-up.

The freezing process on the screen of the wash column in a single stage apparatus originates with the use of pure water to wash the ice crystals emerging from the concentrate. Where the temperature difference of the wash water and the concentrate in the entering slurry exceeds about 9°F, the tendency of the wash column to freeze overtaxes known means for keeping the screen from freezing.

The problem associated with screen freeze-up occurs even in prior art two-stage processes, primarily because heretofore both stages have used pure wash water. Whereas it is normally possible to prevent freeze-up in the stage operating with the dilute concentrate, in the stage operating with the more concentrated concentrate freezing tends to occur. The reason is that, since the freezing point of the highly concentrated concentrate is lower than that of the relatively dilute concentrate, the temperature difference in the wash column handling the more concentrated concentrate is higher.

It is an object of the present invention to provide a method and means for purifying contaminated solvents and simultaneously obtaining dissolved and/or suspended solids in a dry form by a freeze crystallization method that avoids, at least in part, the limitations and disadvantages of the prior art.

It is an object of the invention to provide a two-step method and apparatus for purifying contaminated solvents and simultaneously obtaining dissolved and/or

suspended solids in a dry form which offers advantages over the prior art and in particular has the advantage of avoiding or reducing the very serious problem of solvent freezing on the screen of the wash column, even when the second stage is operated over a temperature range which includes the eutectic freezing point of the liquid treated therein. Features of the invention which assist in achieving this object are: reducing the temperature difference between the wash liquid and concentrate in the affected wash column; reducing the porosity of the second stage ice plug without wash and either omitting to wash the plug of reduced porosity or washing it with reduced amounts of wash liquid.

The invention provides apparatus for purifying contaminated solvent by freeze crystallization comprising:—

(a) a first freezer-crystallizer and wash column sub-assembly for treating contaminated solvent and producing a first concentrate;

(b) a second stage including a second freezer-crystallizer and wash column sub-assembly for treating the said first concentrate and producing in said second wash column a porous plug of substantially pure solvent crystals containing in its interstices a second concentrate;

(c) means for compacting the porous plug as it moves upwards in the wash column to reduce the porosity thereof by applying pressure to it;

(d) means for continually removing upper portions of said porous plug containing said second concentrate;

(e) means for feeding said portions to a melter condenser for producing a solution of low concentration; and

(f) means for returning a part of the low concentration solution to the first stage for reprocessing.

The invention further provides a method of purifying a contaminated solvent by means of a two-stage freezer-crystallizer process, which includes the steps of:—

(a) subjecting as feed liquor a contaminated solvent to a freeze crystallization treatment to form a substantially pure solvent product and a first concentrate;

(b) feeding this first concentrate to the second stage for producing a porous plug of substantially pure solvent crystals containing a second concentrate within the pores thereof;

(c) compacting this porous plug by applying pressure to it to increase its density and to increase the volumetric ratio of solvent crystals to absorbed second concentrate;

(d) continually harvesting an upper portion of the compacted plug and melting

it to form a solution of low concentration;
and

- (e) returning a portion of this solution of low concentration to the first stage for reprocessing with the feed liquor.

The novel features that are considered most characteristic of the invention are set forth in the appended claims; the invention itself, however, both as to its organization and method of operation, together with additional objects and advantages thereof, will best be understood from the following description of a specific embodiment when read in conjunction with the accompanying drawing, the single figure of which is a block representation of a two-stage freeze crystallization water purifying apparatus embodying the principles of the present invention.

- Referring to the drawing the two-stage water purifying apparatus 10 comprises a first freezer-crystallizer 14 and a complementary first wash column 16. The second stage of the apparatus 10 includes a second freezer-crystallizer 18 and its complementary second wash column 20.

In addition to sundry ancillary equipment, which will be described hereinafter, the apparatus 10 includes a first melter condenser 23 and a common heat exchanger 24, which service both stages.

Whereas, typically, the first melter condenser 22 would utilize indirect heat transfer to avoid contaminating the product with volatiles, the second melter condenser 23 may utilize either direct or indirect heat transfer since the volatiles are removed in the first stage.

The process will be generally described in terms of removing salts from aqueous industrial waste. It should be understood, however, that the apparatus and process will work equally well for desalination of sea water or to purify brackish or similar contaminated water or for the purification of liquids in which the solvent is other than water.

The typical known freeze crystallization purifying process may be described by referring to the first stage of the apparatus shown in the drawing. Briefly, the contaminated feed, which may be industrial waste, chemical process streams, brackish water, or sea water, is fed through the heat exchanger 24 to the first freezer-crystallizer 14. The relatively dilute feed mixes with an immiscible secondary refrigerant within the first freezer-crystallizer 14. As the refrigerant evaporates, it cools the feed liquor forming a slurry of pure ice crystals in a relatively dilute concentrate. The slurry is pumped to a cyclone 32 from which a refrigerant-rich ice-free underflow is returned to the first freezer-crystallizer 14. The overflow ice slurry, now relatively free

of refrigerant, is piped to the first wash column 16.

In the wash column, the slurry is separated, in a conventional way, into its pure ice and relatively dilute concentrate components. The pure ice at the top of the first wash column 16 is washed by pure water pumped from the melter condenser 22 by pump 34 to the first wash column 16. The mixture of pure ice and pure water is removed from the wash column and piped to the melter condenser 22. Here the ice is melted. The pure water product is removed through heat exchanger 24.

The one-stage process described above for purifying contaminated water is virtually repeated in a two-stage apparatus. The relatively dilute concentrate produced in the first stage of the two-stage system is piped to the freezer-crystallizer of the second stage as the feed for the second stage (see flow line 36). In a sodium chloride system, the relatively dilute concentrate has a salinity of about 7%. Additionally, the second freezer condenser is preferably at the eutectic freezing point to obtain dissolved or suspended solids in a dry form.

Generally, the problems associated with freeze-up on the screen occurs in the second stage wash column, since the second concentrate produced in this wash column contains a higher percentage of contaminants and, therefore, has a freezing point substantially lower than the freezing point of the relatively dilute concentrate produced in the first stage wash column. Since the second stage wash column in prior art apparatus and methods utilize pure wash water, it follows that there is a greater temperature difference between the pure wash water and the concentrated concentrate in the second stage wash column than occurs between the pure wash water and the relatively dilute concentrate produced in the first stage column. As was pointed out previously, the freezing tendency increases as this temperature difference increases.

The portion of the two-stage apparatus 10 shown in the drawing, incorporating the concept of the present invention, is depicted by the heavy flow lines 40, 41 and 42. Instead of using pure water from the melter condenser 22 to wash the ice plug formed in the second wash column 20, the ice plug in the second wash column is compacted by pressure exerted on the plug by liquid pumped through pipe 42 as described below so that at the top of the second wash column the volume of ice to brine is at least 2 to 1 and, preferably, greater than 3 to 1.

Upper portions of the compacted ice plug are removed by means not shown, e.g. a cutter or scraper, slurried and piped via a

pipe 41 to the second melter condenser 23, where it is converted to a low salinity brine of about five percent or less. A portion of this low salinity brine is pumped via pipe 5 42 through pump 43 and valve 45 to the second wash column 20 and the pressure of the liquid, acting on the porous plug, affects the desired compaction of the plug. The pressure of this liquid at the top of the 10 second wash column 20 is controlled by valve 45, which, therefore, in conjunction with the pump 43, controls the degree of compaction of the porous ice plug in the second wash column 20.

15 The brine that does not mix with the compacted ice plug in the second wash column 20 is removed via screen 21 and returned to the second stage freezer-crystallizer 18. The remainder of the low 20 salinity brine in the second melter condenser 23 is fed via flow line 40 to mix with the feed liquor before the latter enters the first stage freezer-crystallizer 14.

25 This low salinity brine is refluxed to the first stage for potable water production, then back to the second stage for salt harvesting. In this manner, no concentrated reject brine stream is produced. The products of this process are solid salts and 30 potable water. There is no concentrated reject stream to comprise a source of secondary pollution.

Assuming the volumetric ratio of ice to brine in the second melter condenser is 3 35 to 1, the low salinity brine for a sodium chloride system will have a salinity of about 5%. It is possible to decrease the salinity by increasing the pressure at the valve 45 so that the incoming low salinity brine 40 performs a washing function in addition to its previously described compacting function. The low salinity brine that washes the ice crystals in the second wash column, in this mode of operation, tends to increase in 45 salinity and decrease in temperature as it percolates through the ice plug.

The ice washed by the low salinity brine that is removed from the wash column 20 and carried to the second melter condenser, 50 under these conditions, contains a brine a lower salinity than would be present if no washing takes place. Theoretically, this washing action can be increased until the ice removed from the second wash column 55 contains very pure water in the pores. In this case, however, there is a danger that the screen 21 will freeze for the reasons given earlier. Accordingly, the salinity of the low salinity brine using the washing 60 techniques just described, has a lower limit which is determined primarily by energy considerations regarding the amount of power that is necessary to keep the screen from freezing. It follows that the lower 65 salinity limit of the low salinity brine will

depend on the nature of the apparatus and the economic considerations.

Dissolved salts may be removed in the second stage. Salts coming out of solution in the second stage freezer will remain in 70 suspension. The slurry produced in the second freezer-crystallizer is pumped to the cyclone 46. The ice-free underflow from the cyclone 46 comprises a mixture of re- 75 frigerant and concentrate, the latter containing solids in suspension. The refrigerant-rich concentrate is supplied to a solids separator 48 wherein the suspended solids are removed and the refrigerant and remaining liquid is returned 80 via flow line 50 to the second freezer-crystallizer 18. In a similar manner, salts which may precipitate in or prior to the first stage freezer may also be removed.

If a single stage, rather than a multi- 85 stage, cyclone is used, some concentrate will generally be returned to the freezer-crystallizer with the refrigerant or the refrigerant-solid, as the case may be.

The various features and advantages of 90 the invention are thought to be clear from the foregoing description, although variations and modifications of the preferred embodiment illustrated and described are possible. 95

WHAT WE CLAIM IS:—

1. Apparatus for purifying a contaminated solvent by freeze crystallization com- 100 prising:

(a) a first freezer-crystallizer and wash column sub-assembly for treating contaminated solvent and producing a first concentrate; 105

(b) a second stage including a second freezer - crystallizer and wash column sub-assembly for treating the said first concentrate and producing a porous plug of substantially pure 110 solvent crystals containing a second concentrate in the second wash column;

(c) means for compacting the porous plug to reduce the porosity thereof by applying pressure to it; 115

(d) means for continually removing upper portions of said porous plug containing said second concentrate; 120

(e) means for feeding said portions to a melter condenser for producing a solution of low concentration; and

(f) means for returning a part of the low concentration solution to the first stage for reprocessing.

2. Apparatus as claimed in claim 1, 125 wherein the said low concentration solution is returned to the first stage freezer-condenser.

3. Apparatus as claimed in claim 1, 130 wherein the means for compacting of said

porous plug comprises means for causing said low concentration solution to exert pressure on the plug.

4. Apparatus as claimed in claim 3, wherein the means for causing the pressure of the low concentration solution to exert pressure on the porous plug can raise said pressure so that this solution also washes the porous plug to replace the second concentrate with low concentration solution.

- 10 5. Apparatus as claimed in any of the preceding claims, wherein the said second stage includes means for separating solids from the second concentrate.

- 15 6. A method of purifying a contaminated solvent by means of a two-stage freezer-crystallizer process, which includes the steps of:—

- 20 (a) subjecting as feed liquor contaminated solvent to a freeze crystallization treatment to form a substantially pure solvent product and a first concentrate;

- 25 (b) feeding this first concentrate to the second stage for producing a porous plug of substantially pure solvent crystals containing a second concentrate within the pores thereof;

- 30 (c) compacting this porous plug to increase the density thereof and to increase the volumetric ratio of solvent crystals to absorbed second concentrate;

- 35 (d) continuously harvesting an upper portion of the compacted plug and melting it to form a solution of low concentration;

- (e) returning a portion of this solution of

low concentration to the first stage for re-processing with the feed liquor.

7. A method as claimed in claim 6, wherein the ice plug is operated at the eutectic freeze point of the solvent.

8. A method as claimed in claim 6 or claim 7, wherein the plug is compacted so that the volumetric ratio of solvent crystals to second concentrate is at least 2:1.

9. A method as claimed in any of claims 6 to 8, wherein the solvent treated is water.

10. A method as claimed in any of claims 6 to 9, wherein the said solution of low concentration is returned to the plug at a pressure sufficient to compact this plug.

11. A method as claimed in claim 10, wherein the pressure of the solution of low concentration being returned to the plug is sufficiently high to cause this solution to wash the plug and to replace at least a portion of the second concentrate in the plug with the low concentration solution.

12. Apparatus as claimed in claim 1, substantially as herein described with reference to the accompanying drawing.

13. A method as claimed in claim 6, substantially as herein described with reference to the accompanying drawing.

Agents for the Applicants

STANLEY, POPPLEWELL, FRANCIS & ROSS.

Chartered Patent Agents.

20/21 Tooks Court,

Cursitor Street,

London E.C.4A 1LB.

Printed for Her Majesty's Stationery Office by The Tweeddale Press Ltd., Berwick-upon-Tweed, 1976.
Published at the Patent Office, 25 Southampton Buildings, London, WC2A 1AY, from which copies may be obtained.

